

1 603 154

- (21) Application No. 16390/78 (22) Filed 25 Apr. 1978
 (31) Convention Application No. 790727 (32) Filed 25 Apr. 1977 in
 (33) United States of America (US)
 (44) Complete Specification Published 18 Nov. 1981
 (51) INT. CL.³ H01M 6/18
 (52) Index at Acceptance
 H1B 448 450 452 458 618



(54) ELECTROCHEMICAL CELLS WITH SOLID ELECTROLYTES AND ELECTRODES

(71) WE, DURACELL INTERNATIONAL INC., formerly known as P.R. MALLORY & CO., INC., a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 3029 East Washington Street, Indianapolis, Indiana 46206, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described, in and by the following statement:-

This invention relates to high energy density cells utilizing solid electrolytes, solid active metal anodes and novel solid cathodes, and more particularly to such cells in which the cathodes contain an active material which is both ionically and electrically conductive.

Recently the state of electronics has achieved a high degree of sophistication especially in regard to devices utilizing integrated circuit chips, which have been proliferating in items such as quartz crystal watches, calculators, cameras, cardiac pacemakers and the like. Miniaturization of these devices as well as the low power drainage and relatively long lives under all types of conditions has resulted in a demand for power sources which have characteristics of rugged construction, long shelf life, high reliability, high energy density and an operating capability over a wide range of temperatures, as well as concomitant miniaturization of the power source. These requirements pose problems for conventional cells having solution-type or even paste-type electrolytes, especially with regard to shelf-life. The electrode materials in such cells may react with the electrolyte solution and tend therefore to self-discharge after periods of time which are relatively short when compared to the potential life of solid state batteries. There may also be evolution of gases in such cells, which could force the

electrolyte to leak out of the battery seals, thus corroding other components in the circuit, which in sophisticated componentry can be very damaging. To increase the reliability of cell closures increases both bulk and cost, and will not eliminate the problem of self-discharge. Additionally, solution cells have a limited operating temperature range, dependent upon the freezing and boiling points of the solutions contained.

Success in meeting the above demands without the drawbacks of solution electrolyte systems have been achieved with the use of solid electrolyte and electrode cells or solid state cells which do not evolve gases, do not self-discharge on long standing, and have no electrolyte leakage problems. These systems however have had their own particular limitations and drawbacks not inherent in solution electrolyte cells.

Ideally, a cell should have a high voltage, a high energy density, and a high current capability. Prior art solid state cells have however been deficient in one or more of the above desirable characteristics.

A first requirement and an important part of the operation of any solid state cell is the choice of solid electrolyte. In order to provide good current capability a solid electrolyte should have a high ionic conductivity which enables the transport of ions through defects in the crystalline electrolyte structure of the electrode-electrolyte system. An additional, and one of the most important requirements for a solid electrolyte, is that it must be almost solely an ionic conductor. Conductivity due to the mobility of electrons must be negligible because otherwise the resulting partial internal short circuiting would result in the consumption of electrode materials even under open circuit conditions. Solution electrolyte cells include an electronically non-conductive separator between the electrode elements to prevent such a short circuit, whereas solid state cells

50

55

60

65

70

75

80

85

90

utilize the solid electrolyte both as electronic separator and as the ionic conductive species.

High current capabilities for solid state cells have been attained with the use of materials which are solely ionic conductors such as RbAg_4I_5 ($0.27 \text{ ohm}^{-1} \text{ cm}^{-1}$ room temperature conductivity). However these conductors are only useful as electrolytes in cells having low voltages and low energy densities. As an example, a solid state $\text{Ag/RbAg}_4\text{I}_5/\text{RbI}_3$ cell is dischargeable at 40 mA/cm^2 at room temperature but with about 0.012 Whr/c.c. (0.2 Whr/in^3) and an OCV (open circuit voltage) of 0.066V . High energy density and high voltage anodic materials such as lithium are chemically reactive with such conductors, thereby precluding the use of these conductors in such cells. Electrolytes, which are chemically compatible with the high-energy density and high voltage anode materials, such as LiI , even when doped for greater conductivity, do not exceed a room temperature conductivity of $5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$. Thus, high energy density cells with an energy density ranging from about 0.3 to 0.6 Whr/c.c. ($5-10 \text{ Whr/in}^3$) and a voltage of about 1.9 volts for a $\text{LiI/PbI}_2/\text{PbS}$, Pb cell currently being produced are precluded from having an effective high current capability above 50 uA/cm^2 at room temperature. A further aggravation of the reduced current capability of high energy density cells is the low conductivity (both electronic and ionic) of active cathode materials. Conductivity enhancers such as graphite for electronic conductivity and electrolyte for ionic conductivity, while increasing the current capability of the cell to the maximum allowed by the conductivity of the electrolyte, reduce the energy density of the cell because of their volume.

Commercial feasibility in production of the electrolyte material is another factor to be considered in the construction of solid state cells. Thus, the physical properties of electrolytes such as BaMg_5S_5 and BaMg_5Se_6 , which are compatible with a magnesium anode but not a lithium anode, and sodium beta aluminas such as $\text{Na}_2\text{O} \cdot 11 \text{ Al}_2\text{O}_3$, which are compatible with sodium anodes, will preclude the fabrication of cells having a high energy density capability even when costly production steps are taken. These electrolytes have ceramic characteristics making them difficult to work with, especially in manufacturing processes involving grinding and pelletization, with such processes requiring a firing step for structural integrity. Furthermore, the glazed material so formed inhibits good surface contact with the electrodes, with the result of poor conductivity leading to poor cell performance. These electrolytes are thus typically used in cells with molten electrodes.

It is therefore an object of the present invention to increase the conductivity of the cathode of solid state cells in conjunction with high energy density anodes and compatible electrolytes, so that there is an increase in energy density without current capability losses, while maintaining chemical stability between the cell components.

According to the present invention there is provided a solid state electrochemical cell comprising a solid active metal anode, a solid electrolyte comprising at least one active metal salt compatible with said anode and a solid cathode wherein said cathode comprises a compound having an ionic and electronic conductivity of 1×10^{-10} to $1 \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature and being selected from metal hydroxides, metal iodides, non-metal chalcogenides, non-stoichiometric metal oxides, and non-stoichiometric compounds of said anode metal with said metal hydroxides, metal iodides, non-metal chalcogenides and non stoichiometric metal oxides wherein said compound is cathode active and comprises at least 80% by weight of said cathode.

The present invention involves the use as the cathode-active material of a solid state cell of a material which has the characteristics of being both ionically and electronically conductive as well as being able to function as an active cathode material. Normally cathodes require the incorporation of substantial amounts (e.g. over 20 percent by weight) of an ionic conductor such as that used as the electrolyte in order to facilitate ionic flow in the cathode during the cell reaction. This is especially true if the cathodic material is an electronic conductor since otherwise a reduction product would form at the cathode-electrolyte interface which would eventually block off a substantial amount of the ionic flow during discharge. However the incorporated ionic conductors in prior art cells have not in general been cathode active materials, with the result of significant capacity loss. Additionally, cathode active materials which are poor electronic conductors require the further incorporation of electronically conductive materials, which further reduces the cells energy capacity. By combining the functions of electronic and ionic conductivity with cathode activity in accordance with this invention, a higher energy density and current capability are attained, with the need for space wasting conductors being obviated. Thus cells having ionically and electronically conductive cathode active material will not generally require the substantial inactive conductive materials generally required for maintaining cell performance in prior art cells. The conductive active cathode materials comprise at least 80% by weight of the entire cathode thereby substantially increasing the energy density of the cell without

concomitant loss of cell performance.

Examples of materials having the requisite characteristics of ionic and electronic conductivity and which are cathodically active as well as being compatible with electrolytes used in high energy density cells include the non stoichiometric forms of metal oxides having ideal stoichiometries such as MnO_2 , TiO_2 , MoO_3 , Ta_2O_5 , V_2O_5 and WO_3 . The non stoichiometric metal oxides have the requisite electronic conductivity whereby the need for non-cathode-active electronic conductors can be reduced or eliminated. Stoichiometric metal oxides on the other hand have insulative properties making them unsuitable. Other cathode active materials having the requisite conductivities include metal iodides such as CdI_2 , FeI_2 , GeI_2 , MnI_2 , TiI_2 , TlI_2 , VI_2 , and YbI_2 ; metal hydroxides such as $Cd(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$, and $Ni(OH)_2$; and non-metal chalcogenides such as $SiTe$ and CS_n wherein "n" is 0.001 to 1.0 and is made in the manner described in Australian Journal of Chemistry Vol. 0 (1956) p.201-205.

Also included are the non-stoichiometric compounds such as Na_xWO_3 where $x < 1$, which to some extent contain the complexed form of one of the cathode materials with the anodic cation and which are believed to be intermediate reaction products during cell discharge. The non-stoichiometry engendered by complexing with the anode cation is different from and may be in addition to the non-stoichiometry of the metal oxides described above.

In order for the ionically and electronically conductive, cathode-active material to be commercially useful in high voltage cells such as those with lithium anodes, it should preferably be able to provide with lithium a voltage couple having an open circuit voltage (O.C.V.) of 1.5 volts and most preferably above 2 volts.

A further criterion for the cathodic material is that both the ionic and electronic conductivities of the cathode-active material should range between 10^{-10} and $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$, with a preferred ionic conductivity of more than 10^{-6} and an electronic conductivity greater than 10^{-3} , all at room temperature.

In addition, and most importantly, the ionically and electronically conductive, active cathode material must be compatible with the solid electrolytes used in the high energy density cells.

The solid electrolytes used in high energy density lithium cells are lithium salts and have ionic conductivities greater than $1 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature. These salts can either be in the pure form or combined with conductivity enhancers such that the current capability is improved thereby. Examples of lithium salts having the requisite conductivity for satisfactory cell utilization

include lithium iodide (LiI), and lithium iodide admixed with lithium hydroxide ($LiOH$) and aluminium oxide (Al_2O_3), the latter mixture being referred to as LLA and being disclosed in U.S. patent No. 3,713,897.

High energy density solid electrolyte cells may have as their anodes materials similar to lithium which have high voltage and low electrochemical equivalent weight characteristics. Suitable anodic materials include metals from groups IA and IIA of the Periodic Table such as sodium, potassium, beryllium, magnesium and calcium as well as aluminium from Group IIIA and other metals above hydrogen in the EMF series.

Cells with active metal anodes other than lithium can utilize corresponding salts as electrolytes, such as sodium salts for a cell with a sodium anode. Additionally, electrolyte salts with useful conductivities and having a cation of a metal of a lower EMF than that of the anode metal may also be useful.

It is postulated that the aforementioned ionically and electronically conductive cathode-active materials react with the ions of the anode (e.g. lithium cations) to form a non-stoichiometric complex during the discharge of the cell. This complexing of cations allows them to move from site to site thereby providing ionic conductivity. Additionally, the above compounds provide the free electrons necessary for electronic conductivity.

A limiting factor in solid state cell performance is the conductivity of the cell reaction product. A low conductivity product results in large internal resistance losses which effectively terminate cell usefulness. Thus, in cells having the above ionically and electronically conductive, cathode-active material the complexed reaction product retains conductivity thereby enabling full utilization of unreacted cathode materials which are in proximity therewith.

A small amount of electrolyte can also be included in the cathode structure in order to blur the interface between cathode and electrolyte, thereby providing more intimate electrical contact between the cathode and the electrolyte. This enables the cell to operate at higher current drains for longer periods of time. Additionally the electrolyte inclusion can increase the ionic conductivity of the cathode if the ionically conductive cathode active material has a lower conductivity than that of the electrolyte. This inclusion however, if made, should preferably not exceed 10% by weight since greater amounts would merely decrease the energy density of the cell with very little if any further improvement of current drain capacity. Additionally, small amounts of an electronic conductor may also be added to increase electronic conductivity. However,

the total percentage by weight of conductivity enhancers should not exceed 20% of the cathode.

In order that the present invention may be more completely understood the following example is given in which all parts are parts by weight unless otherwise specified. The example is for illustrative purposes only and should not be interpreted as providing limitations to the present invention.

EXAMPLE

A solid state cell made from a lithium metal disc having the dimensions of about 1.47 cm² surface area by about 0.01 cm thickness; a cathode disc of the dimensions of about 1.71 cm² surface area by about 0.02 cm thickness consisting of 85% WO₃, 5% carbon black and 10% LLA, and weighing 200 mg; and a solid electrolyte therebetween with the same dimensions as the cathode and consisting of LiI, LiOH, and Al₂O₃ in a 4:1:2 ratio was assembled in the following manner. The electrolyte was first pressed with the cathode at a pressure of about 6.8 x 10⁸ N/m² (100, 000 psi). Then the anode was pressed thereto using about 3.4 x 10⁸ N/m² (50,000 psi). The resulting cell was discharged at 95°C under a load of 20 kΩ. The cell produced 8 milliamp hours (maH) to 2 volts, about 15 mAH to 1.5 volts, and about 30 mAH to 1 volt.

WHAT WE CLAIM IS:

1. A solid state electrochemical cell comprising a solid active metal anode, a solid electrolyte comprising at least one active metal salt compatible with said anode and a solid cathode wherein said cathode comprises a compound having an ionic and electronic conductivity of 1 x 10⁻¹⁰ to 1 x 10² ohm⁻¹ cm⁻¹ at room temperature and being selected from metal hydroxides, metal iodides, non-metal chalcogenides, non-stoichiometric metal oxides, and non-stoichiometric compounds of said anode metal with said metal hydroxides, metal iodides, non-metal chalcogenides and non stoichiometric metal oxides wherein said compound is cathode active and comprises at least 80% by weight of said cathode.
2. The solid state electrochemical cell of claim 1 wherein said compound is selected from non-stoichiometric MnO₂, TiO₂, MoO₃, Ta₂O₅, V₂O₅, and WO₃; CdI₂, FeI₂, GeI₂, MnI₂, TiI₂, TlI₂, VI₂, YbI₂, Cd(OH)₂, Fe(OH)₂, Mn(OH)₂, Ni(OH)₂, CS_n where n is 0.001 to 1, and SiTe₂.
3. The solid state electrochemical cell of claim 1 or 2 wherein said anode metal is lithium.
4. The solid state electrochemical cell of claim 1, 2 or 3 wherein said electrolyte comprises lithium iodide.
5. The solid state electrochemical cell of claim 4 wherein said electrolyte further includes lithium hydroxide and aluminum

oxide.

6. The solid state electrochemical cell of claim 5 wherein said compound is non-stoichiometric WO₃.

7. The solid state electrochemical cell of claim 1 wherein said compound is the non-stoichiometric compound Na_xWO₃ wherein x<1, and said anode metal is sodium.

8. The solid state electrochemical cell of any preceding claim wherein said ionic conductivity is more than 10⁻⁶ ohm⁻¹ cm⁻¹ and said electronic conductivity is greater than 10⁻³ ohm⁻¹ cm⁻¹.

9. A solid state electrochemical cell as claimed in claim 1 and substantially as herein described.

10. A solid state electrochemical cell substantially as set forth in the foregoing example.

MARKS & CLERK
Chartered Patent Agents
Agents for the Applicants

Printed for Her Majesty's Stationery Office,
by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings,
London, WC2A 1AY, from which copies may be obtained.